



# Some views about indoor air photocatalytic treatment using TiO<sub>2</sub>: Conceptualization of humidity effects, active oxygen species, problem of C<sub>1</sub>–C<sub>3</sub> carbonyl pollutants

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## ABSTRACT

This overview of photocatalytic purification/deodorization of indoor air using TiO<sub>2</sub> includes four parts. First, considering that TiO<sub>2</sub> exposed to indoor air – which contains several thousands ppmv of water – is covered by layers of water molecules, it is suggested that: (i) the approach to the surface of pollutants at ppbv concentrations is hindered, (ii) the pollutants are not dissociated by mere adsorption, (iii) •OH radicals are formed by mechanisms identical to those proposed for TiO<sub>2</sub> exposed to liquid water, and (iv) •OH radicals are mobile within the adsorbed water layers. Second, the formation and role of superoxide, singlet molecular oxygen and labile surface oxygen atoms of TiO<sub>2</sub> are reviewed. Third, the competition between pollutants at ppbv levels for elimination under usual conditions of purifiers is discussed. Fourth, the question of the effect of indoor air photocatalytic treatment on the average concentration of low-molecular-mass carbonyls is addressed.

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## 1. Introduction

Photocatalysis over TiO<sub>2</sub> is one of the technologies that can be envisaged to purify/deodorize air. Indeed, indoor air cleaners based on this technology – often together with the adsorption on activated carbon – are commercialized. Basic information on photocatalysis, including air treatment, can be found, for example, in a book [1] and an overview [2]. Photocatalytic air cleaning has been evaluated [3,4]. Many investigations have dealt with the main factors susceptible of improving the photocatalytic efficacy, among which: the optimization of the incident irradiance on TiO<sub>2</sub>, the type of TiO<sub>2</sub>, the methods for coating TiO<sub>2</sub> onto fixed supports of various kinds and shapes (e.g. [5–26]).

However, in studies of the photocatalytic removal of pollutants in indoor air, an aspect that is relatively often not sufficiently taken into account is that pollutants are present at concentrations ranging from fractions of ppbv to some tens of ppbv (e.g. [27,28]), with the exception, however, of CO and CH<sub>4</sub> whose concentration reaches a few ppmv (CO<sub>2</sub> is a particular case because it is not a hazardous compound at its usual concentration around 350 ppmv and it is stable). By contrast, the concentration of water vapor is between 3600 and 20,000 ppmv indoors. In other words, the surface of a semi-

conductor oxide, such as TiO<sub>2</sub>, exposed to air is covered by water molecules. Consequently, the interactions to be considered are not those between “dry” TiO<sub>2</sub> and pollutants in the ppmv domain as in most laboratories studies, but those between TiO<sub>2</sub> covered by layers of water and pollutants in the ppbv domain.

On the other hand, the intermediate products of organic pollutants at the near-end of their respective photocatalytic degradation chain can be the same. As a result, the concentrations of these low-mass – hence often relatively volatile compounds – can increase significantly in spite of the very low concentrations of the original pollutants because of the high number of these pollutants. Therefore, these concentrations must be thoroughly measured under conditions corresponding closely to those of the use for which the photocatalytic purifier has been designed.

In this paper, starting from the present knowledge about liquid water and adsorbed water layers on TiO<sub>2</sub>, consequences of the exposure of TiO<sub>2</sub> to humid air for the approach of pollutants to the surface, the adsorption modes of pollutants, and the formation and mobility of •OH radicals are first discussed. Then, the potential roles in photocatalytic oxidations of various oxygen species, viz. superoxide, singlet molecular oxygen and labile surface oxygen atoms of TiO<sub>2</sub>, are examined. The question of the interference between air pollutants at ppbv levels regarding their photocatalytic removal is also addressed. Finally, the potential danger linked to some gas-phase intermediate products of photocatalytic degradation is considered.

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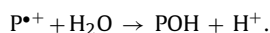
## 2. How can indoor air humidity hinder the approach of pollutants to TiO<sub>2</sub>?

The interaction of TiO<sub>2</sub> and other solid oxides with water via hydrogen bonds has been investigated long ago [29]. Schematically, H<sub>2</sub>O can be H-bound to the several types of OH surface groups which can also be H-bound to each other. The coverage in OH surface groups and hence in water molecules obviously depends on the characteristics of the TiO<sub>2</sub> sample. Because of these H-bonds the adsorbed H<sub>2</sub>O molecules are arranged (with distortions) more rigidly than in liquid water. The effect of the surface can extend over several molecular layers with progressive changes in the water network [30]. For instance, calculations have shown that for the 101 plane of anatase, the variation in the adsorption enthalpy is –67 kJ/mol for the first water layer against –51 kJ/mol for the second water layer [31]. Simulations of the trajectories of water molecules at 160 K on the 101 plane of anatase have shown that, with respect with the third water layer, the motions of the water molecules are markedly restricted not only in the first layer but also in the second layer [32].

Therefore, to approach the TiO<sub>2</sub> surface, pollutants must break H-bonds between water molecules whose strength near the surface is significantly higher than in bulk water. The attraction forces between the pollutants and TiO<sub>2</sub> are diminished by the presence of the well-organized network of adsorbed water layers. For organic molecules that can form H-bonds with water, the water molecules that are not H-bound to the organic form a kind of “cavity” around the organic compound [33]. They interact with fewer other water molecules of the network. This means an organic-size dependent breaking of water H-bonds. In other terms, the presence of this type of pollutant disorganizes the water network. In the case of organic molecules that are not capable of forming H-bonds with water, the adsorbed water layers constitute a kind of barrier hindering their contact with TiO<sub>2</sub> because the reorientation of water molecules – particularly those close to the surface – around these non-polar pollutants, such as hydrocarbons, is very unfavorable considering the associated change in entropy [34].

This fundamental reasoning allows one to explain qualitatively, for instance in the case of acetone, both the very detrimental effect of water vapor upon the adsorbed amount of this organic on TiO<sub>2</sub> and the negligible effect of acetone pressure upon water adsorption [5], because the approach of acetone to the surface is hindered in spite of the possibility for acetone to form H-bonds with water molecules. Also, measurements have shown that chlorobenzene, which is insoluble in water, did not adsorb significantly on TiO<sub>2</sub> previously exposed to water vapor [35].

Although it has, on one hand, an unfavorable role on the photocatalytic removal of pollutants – because it prevents the access of pollutants to TiO<sub>2</sub> as aforementioned – adsorbed water can be needed, on the other hand, in both the hydrolysis of certain pollutants and the transformation of organic radical-cations, P<sup>•+</sup>, resulting from electron transfer from electron-rich pollutants to photo-excited TiO<sub>2</sub>; in that latter case, adsorbed water can act as a nucleophile:

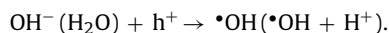


Water can also be a source of •OH radicals (see Section 3). These various effects explain why the variations in the elimination rates of pollutants as a function of the air humidity depend on the pollutant.

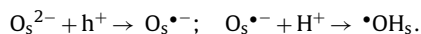
## 3. How can •OH radicals be formed when TiO<sub>2</sub> is exposed to humid air?

The formation of •OH radicals at the surface of UV-irradiated TiO<sub>2</sub> in liquid water has been proposed long ago [36]. It is sup-

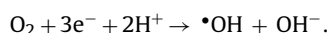
posed to occur by several pathways whose relative importance is still debated [37]. It may arise from direct electron transfer from photo-excited TiO<sub>2</sub> to adsorbed OH<sup>–</sup> ions and water molecules:



Location of a hole at a surface oxygen anion and protonation of the resulting radical-anion can also be envisaged [37]:



If these latter reactions take place at labile surface oxygen anions, detachment of the •OH<sub>s</sub> radicals from the surface could occur. Three-electron reduction of O<sub>2</sub> (via O<sub>2</sub><sup>•–</sup>/HO<sub>2</sub><sup>•</sup> and H<sub>2</sub>O<sub>2</sub>) has also been proposed from analogy with the reactions assumed to exist in liquid water in the absence of TiO<sub>2</sub> according to the overall reaction:



It is not unlikely that these various reactions can also happen on TiO<sub>2</sub> exposed to humid air, given the existence of adsorbed water layers.

## 4. Potential mobility of •OH radicals within the adsorbed water layers

Whereas for pollutants the approach to TiO<sub>2</sub> is restricted by the adsorbed water layers, it can be envisaged, from the simple viewpoint of chemical structure, that •OH radicals photogenerated in TiO<sub>2</sub> can migrate into the adsorbed water layers. Indeed, a •OH radical can easily replace a H<sub>2</sub>O molecule in the adsorbed water network. This replacement implies relatively small variations in length of the hydrogen bonds [38,39]. Accordingly, it can be assumed that changes in hydrogen bonds to accommodate a •OH radical can easily result from molecular rotations of the water molecules [38,39]. It has been calculated that in liquid water at ambient temperature about 20% of the H-bonds between water molecules are broken at a given time [38]. Indeed, water molecules switch partners between themselves frequently, owing to the molecular rotations [40–42] which occur in times on the order of 700 fs [41]. Also, it has been calculated that a (H<sub>2</sub>O)<sub>8</sub> cluster can be transformed into a •OH(H<sub>2</sub>O)<sub>7</sub> cluster by replacing a H<sub>2</sub>O molecule by a •OH radical at one of the corner of the cubic-like octahedral structure without changing this structure [43].

In summary, because a •OH radical can create H-bonds and its size differs only slightly from that of H<sub>2</sub>O, the reorientation or restructuring of the H-bound water molecules is minimal when •OH radicals are introduced into the water network. It ensues that the mobility of •OH radicals within the adsorbed water layers could understandably be much higher than those of pollutants. This mobility could contribute to the removal of pollutants that cannot easily approach the TiO<sub>2</sub> surface. The studies cited above [38,39,43] provide a basis to conceptualize the possibility for the •OH radical to react at some distance from the surface when TiO<sub>2</sub> is in contact with liquid water [44–49] or covered by adsorbed water layers because of the humidity of air as is suggested here.

Note that the formation of •OH radicals is supposed to result from the oxidation of adsorbed H<sub>2</sub>O molecules and the reduction of H<sub>2</sub>O<sub>2</sub> molecules formed on the surface of TiO<sub>2</sub> (see Section 3). Consequently, the surface-formed •OH radicals should be linked to TiO<sub>2</sub> by weak H-bonds as are these molecules. Because the adsorbed water layers contain indistinguishable water molecules to which the •OH radicals can indifferently be bound, the mobility of the •OH radicals within these layers should require energy only on the order of that allowing the rotations of the water molecules which induce the breaking of H-bonds, as is discussed in the next-to-last paragraph.

However, because the mobility of  $\bullet\text{OH}$  radicals within the well-organized network of adsorbed water layers is expected to be lower than in bulk water, the properties of  $\bullet\text{OH}$  radicals influenced by the surface should be somewhat different from those of the so-called free  $\bullet\text{OH}$  radicals, which can be generated in liquid water by various processes, such as, for example the UV-C irradiation of  $\text{H}_2\text{O}_2$ .

## 5. Adsorption modes of organic pollutants on $\text{TiO}_2$ exposed to humid air

In a photocatalytic purifier of indoor air, the  $\text{TiO}_2$ -containing coating remains very likely around room temperature, the potential heating by the UV lamps being at least partially compensated by the air flow at a high rate over or through the coating. Consequently, no  $\text{TiO}_2$  activation due to a substantial raise in temperature above the ambient is expected. Moreover,  $\text{TiO}_2$  is covered by water layers (see Section 2). As a result, there are, in principle, no surface sites capable of dissociating the molecules of pollutants before their attack by photocatalytically generated active species.

In laboratory studies aiming at determining the adsorption modes of molecules of pollutants, dehydrated or even dehydroxylated  $\text{TiO}_2$  has been used, in particular for experimental reasons, infrared spectroscopy often being the examination technique chosen. Therefore, the adsorbed species found under these “dry” conditions may not exist for  $\text{TiO}_2$  exposed to humid air. It is probably the case for low-molar-mass alcohols which have been reported to give rise to alkoxides on “dry”  $\text{TiO}_2$  [50–53]. Accordingly, the degradation pathways from alkoxides may not be relevant for the purification of indoor air.

Much attention has also been paid to the adsorption modes of carboxylic acids (principally, formic and acetic acids), especially because they are intermediate products of the photocatalytic degradation of nearly all organic pollutants. Again, most studies have dealt with “dry”  $\text{TiO}_2$ . In that case, surface carboxylates were easily detected by infrared spectroscopy (e.g. [54]), but their involvement in photocatalytic reactions occurring in purifiers of indoor air seems problematic.

To conclude, in line with the conceptualization of Section 2, it is suggested that the organic pollutants in the ppbv domain remain undissociated in the adsorbed water layers and at the surface until they encounter an active species arising from the photo-activation of  $\text{TiO}_2$ .

## 6. Oxygen species formed or becoming labile when $\text{TiO}_2$ is photo-activated

### 6.1. Superoxide

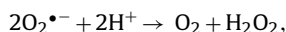
Because  $\text{O}_2$  is an electrophilic compound (electron affinity:  $0.44\text{ eV} = 42.45\text{ kJ/mol}$ ), the formation of superoxide,  $\text{O}_2^{\bullet-}$ , on  $\text{TiO}_2$  submitted to UV irradiation has been investigated long ago. For that, ESR is an especially relevant technique. Indeed, an ESR signal assigned to  $\text{O}_2^{\bullet-}$  was reported as early as in 1971 when UV-irradiated  $\text{TiO}_2$  was exposed to  $\text{O}_2$  at room temperature [55]. The protonated form  $\text{HO}_2^\bullet$  was also detected by ESR at 77 K for “hydrated” UV-irradiated  $\text{TiO}_2$  [56]. In another early work [36], it was shown that the photoadsorption of  $\text{O}_2$  was enhanced by water vapor; it was suggested that water decreases the recombination rate of photoproducted charge carriers by scavenging holes and therefore increases the number of electrons available to be captured by  $\text{O}_2$  to yield  $\text{O}_2^{\bullet-}$ . The formation of  $\text{O}_2^{\bullet-}$  has been repeatedly demonstrated by ESR studies over the years (e.g. [10]) and it has been reviewed [57].

Indeed, scavenging of photogenerated electrons by  $\text{O}_2$  can be challenged by  $\text{O}_3$  which has a much higher electron affinity:

$2.1\text{ eV} = 202.6\text{ kJ/mol}$ . To interpret the enhancement of photocatalytic oxidations in the presence of non-photo-excited ozone, it has been suggested [58,59] the formation of  $\text{O}_3^{\bullet-}/\text{HO}_3^\bullet$  which is assumed to readily decompose into  $\text{O}_2$  and  $\bullet\text{OH}$ .

In principle, superoxide is considered as poorly reactive, that is, it is not supposed to react directly with chemical pollutants. This absence of significant reactivity is well-documented, in particular in a review [60] with a provocative title: How super is superoxide? The lack of reactivity of  $\text{O}_2^{\bullet-}$  formed by photo-excitation of  $\text{TiO}_2$  was in fact illustrated long ago; the  $\text{O}_2^{\bullet-}$  ESR signal was not affected by subsequently exposing the  $\text{TiO}_2$  sample to gaseous methylpropane (isobutane) in the dark [55].

However, experiments with superoxide dismutase (SOD), an enzyme that dismutates superoxide according to the overall reaction

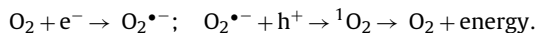


have pointed to a favorable chemical role of  $\text{O}_2^{\bullet-}$  in photocatalytic oxidation reactions [61–65]. Although these experiments were carried out in aqueous  $\text{TiO}_2$  suspensions, they can be thought to be relevant to photocatalytic oxidation reactions in air as the surface of  $\text{TiO}_2$  is covered by layers of water (see Section 2). Two types of experiments have shown that the detrimental effect of SOD was really due to the enzymatic activity and not to a mere competition between the degradation of the target pollutant and that of the organic structure of SOD. First, at equal percentages of removal of the appropriately selected target pollutant, distinct distributions of products were observed with and without SOD [64,65]. Most importantly, if the SOD activity was inhibited by complexation of the SOD  $\text{Cu}^{n+}$  ions, the SOD effect on the photocatalytic rate was suppressed [63].

It has been proposed that  $\text{O}_2^{\bullet-}$  can react with the radical-cations formed by direct electron transfer from certain pollutants to the valence band of photo-excited  $\text{TiO}_2$  [64]. To prove that, the first step is to choose a compound whose degradation primary products allow discriminating between  $\bullet\text{OH}$ -induced and  $\text{h}^+$ -induced pathways. The products of this compound obtained by photocatalysis are compared to those issued from a process whose active species are  $\bullet\text{OH}$  radicals, such as the photo-Fenton and the  $\text{H}_2\text{O}_2$ -UV processes. It is, of course, essential to adjust the characteristics of these processes to make the comparison at approximately equal removal of the compound. SOD can be used to determine that  $\text{O}_2^{\bullet-}$  is really involved chemically [64]. Finally, if the addition of  $\text{O}_2^{\bullet-}$  to the radical-cation is supposed to form a 1,2-dioxetane intermediate, proper substitution at the positions where  $\text{O}_2^{\bullet-}$  is thought to add will validate the hypothesis of the formation of this intermediate by inhibiting this addition and thereby support the existence of the whole mechanism [65].

### 6.2. Singlet molecular oxygen

The existence of singlet molecular oxygen,  $^1\text{O}_2$ , on UV-irradiated  $\text{TiO}_2$  has been proposed [66–71]. Formation of  $^1\text{O}_2$  might result from the reaction of superoxide with a photogenerated hole.  $^1\text{O}_2$  would subsequently yield  $\text{O}_2$  with an energy release of about  $1\text{ eV}$  (or  $\sim 96.5\text{ kJ/mol}$ ) [68]. In other words,  $^1\text{O}_2$  would be an intermediate entity in the course of an electron-hole recombination involving one molecule of  $\text{O}_2$ :



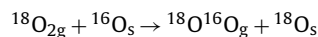
Possible evidence for the existence of  $^1\text{O}_2$  has been drawn from three main types of observations. First, the detection of products thought to be exclusively formed by reaction with  $^1\text{O}_2$  has been found using probe molecules. However, the specificity of these probes is disputed. Second, for  $\text{TiO}_2$  in aerated liquid ethanol,

an ESR signal has been attributed to  $^1\text{O}_2$  [68], but its origin is debated. Third, very weak phosphorescence at 1270 nm has been attributed to  $^1\text{O}_2$  for an aqueous  $\text{TiO}_2$  suspension [69–71]. The apparent quantum yield of this phosphorescence was as high as 0.2 for  $\text{TiO}_2$  Degussa P-25 [70]. Moreover, this phosphorescence varied as the concentration in superoxide under various conditions, which is consistent with the formation of  $^1\text{O}_2$  from  $\text{O}_2^{\bullet-}$  as aforementioned [71]. In the same study, the involvement of  $^1\text{O}_2$  in photocatalytic oxidations has been deduced from the acceleration of the phosphorescence decay in the presence of pyrrole and amino-acids or proteins, such as methionine ((2S)-2-amino-4-methylsulfanylbutanoic acid), folic acid and collagen [71]. Until now, these observations seem to be the most convincing evidence regarding the formation and role of  $^1\text{O}_2$ , but this evidence relies on the correct attribution of the phosphorescence signal.

Although none of these experiments refers to the gas phase, they may be relevant to  $\text{TiO}_2$  exposed to humid air and hence covered by water layers.

### 6.3. Can O atoms of $\text{TiO}_2$ participate in photocatalytic oxidations?

The oxygen isotope exchange (OIE) between gaseous  $^{18}\text{O}_2$  and photo-excited  $\text{Ti}^{16}\text{O}_2$  [72–74,76–85] (or other unlabeled semiconducting oxides, such as  $\text{Zn}^{16}\text{O}$  [75]) has been used to demonstrate the lability of O atoms of  $\text{TiO}_2$ . It occurs according to the overall reaction:



showing that, for each OIE event, a  $^{16}\text{O}$  atom of the solid surface is removed to form  $^{18}\text{O}^{16}\text{O}$ , initially adsorbed and then released into the gas phase, while one of the atoms of  $^{18}\text{O}_2$  is left on the surface.

It is obvious that OIE via this overall reaction involves the splitting of  $^{18}\text{O}_2$  and the removal of a  $^{16}\text{O}$  atom from  $\text{Ti}^{16}\text{O}_2$ . This removal is evidently favored by surface irregularities, i.e., coordinatively unsaturated  $^{16}\text{O}$  atoms which are more labile [83]. In that sense, OIE can be regarded as a method for probing surface irregularities. That is important considering the role of these irregularities in the recombination rate of photogenerated charge carriers and hence in photocatalytic efficacy. It is expected that the location of a photogenerated hole at a surface  $\text{O}^{2-}$  anion to formally produce an  $\text{O}^{\bullet-}$  species would lower the strength of the corresponding Ti–O bond.

The splitting of  $^{18}\text{O}_2$  may arise from the capture of a photo-generated electron by adsorbed  $^{18}\text{O}_2$ , thus forming  $^{18}\text{O}_2^{\bullet-}_{\text{ads}}$  (see Section 6.1). Indeed, the added electron is located in an antibonding orbital, so that the O–O bond strength is decreased as illustrated by the increase in O–O bond length from  $\sim 0.122$  nm for gaseous  $\text{O}_2$  to  $\sim 0.137$  nm for free  $\text{O}_2^{\bullet-}$  [86]. According to a scheme previously published [85],  $^{18}\text{O}^{16}\text{O}_{\text{ads}}$  is then formed by isotopic exchange between a labile  $^{16}\text{O}_{\text{s}}$  atom and  $^{18}\text{O}_2^{\bullet-}_{\text{ads}}$ .

It has been reported that OIE was not observed in the presence of methylpropane (isobutane) and becomes observable once this alkane had disappeared from the gas phase [76]. This observation can be explained by the preferential reaction of  $^{18}\text{O}_2$  with the radical  $(\text{CH}_3)_3\text{C}^{\bullet}$  resulting from the abstraction of the labile H atom of  $(\text{CH}_3)_3\text{CH}$  by a photoproduct  $\bullet\text{OH}$  radical. Because the main product, acetone, was not detected in the gas phase under the conditions used, the fate of the  $^{18}\text{O}$  atoms could not be determined [76]. By contrast, in a study [84] of the photocatalytic oxidation of  $\text{CH}_3\text{Cl}$  by  $^{18}\text{O}_2$  on the 110 face of a  $\text{Ti}^{16}\text{O}_2$  rutile single crystal, CO and HCHO could be detected in the gas phase as a result of both their volatility and the low surface area of the single crystal. CO contained only  $^{18}\text{O}$  and HCHO was predominantly labeled with  $^{18}\text{O}$ . From these analyses, it was deduced that lattice  $^{16}\text{O}$  plays a minor role in the oxidation of  $\text{CH}_3\text{Cl}$  as compared with gaseous  $^{18}\text{O}_2$ .

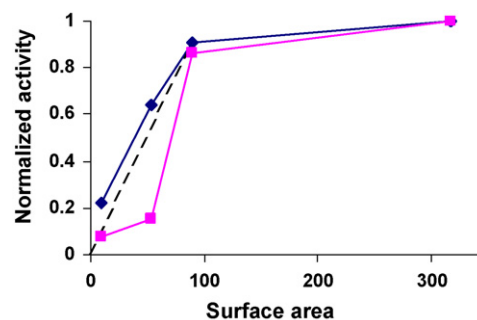
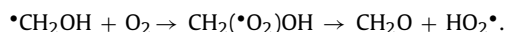
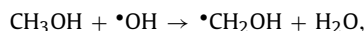


Fig. 1. Activity of the  $\text{TiO}_2$  PC samples for methanol removal (diamonds) and oxygen isotope exchange (squares), normalized to the highest activity, against the  $\text{TiO}_2$  surface area in  $\text{m}^2 \text{g}^{-1}$ .

Further evidence of this minor role was drawn from a comparison of OIE with the removal of gaseous methanol over the same  $\text{TiO}_2$  samples [85]. These commercially available samples (Cristal-Millennium Chemicals) were prepared from  $\text{TiOSO}_4$  by sintering at increasing temperatures in the order: PC500 (not sintered gel), PC105, PC50, and PC10. Their absorption around 365 nm (the main emission wavelength of the mercury lamp employed) was almost equal with the exception of that of PC10 which was significantly higher; however, as PC10 was the less active sample at equal  $\text{TiO}_2$  mass for both OIE and methanol removal, this difference in absorption cannot be the factor explaining the ranking of the photocatalytic activities. Methanol was selected for the comparison with OIE because the formation of its primary product, HCHO, does not need the incorporation of an O atom as shown by the following predominant chemical equations, the last one corresponding to the slow, spontaneous decomposition of the intermediate peroxy radical [87]:



The OIE mechanism was the same for all  $\text{TiO}_2$  samples. Moreover, the initial OIE rate varied almost linearly with the starting  $^{18}\text{O}_2$  pressure in the range investigated (1–100 Pa) [88]. This is important since it means that the ranking of the initial OIE rates was really meaningful because it was the same irrespective of the  $^{18}\text{O}_2$  pressure used for the tests.

For both OIE and methanol removal, the ranking of the activities of the  $\text{TiO}_2$  samples at equal  $\text{TiO}_2$  mass was the same [85]: PC500 (317) > PC105 (85–95) > PC50 (54) > PC10 (10). The numbers in parentheses indicating the surface area,  $S$ , in  $\text{m}^2 \text{g}^{-1}$ , show that the activities decreased with decreasing  $S$ . That is not surprising since the amount of adsorbed  $\text{O}_2$  also decreased for an equal  $\text{TiO}_2$  mass in the reactor. However, the activities were not at all proportional to  $S$  (Fig. 1). In fact, sintering not only decreases  $S$ , but is also expected to decrease the density in bulk and surface irregularities. The resulting restructuring decreases both the recombination rate,  $k_r$ , of photoproduct charges – which enhances the photocatalytic activity – and the lability,  $L$ , of surface O atoms, which can be detrimental to the photocatalytic activity. Therefore, the net effect of sintering on the photocatalytic activity is the result of a balance between  $S$ ,  $k_r$  and  $L$ . One would expect the changes in  $S$  and  $k_r$  to affect similarly both OIE and methanol removal, and the change in  $L$  to affect these reactions very differently, since  $L$  is a prerequisite for OIE and should augment only marginally the methanol removal rate if the surface O atoms play a minor role in the oxidation of methanol.

The complex variations of the photocatalytic activities of  $\text{TiO}_2$  samples sintered at different temperatures for both OIE and



methanol removal is shown by the plot of these activities against  $S$  (Fig. 1). A decrease in  $S$  by a factor 3.5 in going from PC500 ( $317 \text{ m}^2 \text{ g}^{-1}$ ) to PC105 ( $85\text{--}95 \text{ m}^2 \text{ g}^{-1}$ ) caused a decrease in activity by a factor of about 1.1 and 1.15 only for methanol removal and OIE, respectively. These small variations suggest that the decrease in  $S$  was almost compensated by a substantial increase in  $k_r$ . Indeed, from measurements by time resolved microwave conductivity [88], it has been inferred that  $k_r$  increases markedly when PC500 is sintered to produce PC105. By contrast, this sintering affected  $L$  only slightly as can be deduced from the weak difference between the variations in the normalized activities of the two reactions. These deductions lead to another one, that is, that  $k_r$  depends on various characteristics of  $\text{TiO}_2$ , such as bulk irregularities (influencing the crystallinity), which are not reflected in the density of labile surface O atoms. Sintering at higher temperatures produced a relatively monotonic but marked decrease in the activity for methanol removal. However, the effect of the decrease in  $S$  was partially counterbalanced by a decrease in  $k_r$  as shown by the fact that the activity was not strictly proportional to  $S$  as illustrated by the dotted line in Fig. 1. The plot for OIE differed very markedly from that for methanol removal: in going from PC105 ( $85\text{--}95 \text{ m}^2 \text{ g}^{-1}$ ) to PC50 ( $54 \text{ m}^2 \text{ g}^{-1}$ ),  $S$  was decreased by a factor of about 1.7, whereas the OIE rate dropped by a factor of about 5.7, suggesting that  $L$  decreased very much. That important decrease in  $L$  was not reflected in the methanol removal rate whose decrease was more regular, as was expected if surface O atoms play only a minor part in the oxidation of methanol.

To address the question of the role of surface  $^{16}\text{O}$  atoms in photocatalytic reactions, an interesting investigation [89] was carried out without the use of labeled  $\text{O}_2$ . The strategy was the following. First, the selected reaction was the oxidation of  $\text{HCOOH}$  because no intermediate products are thought to be formed. Second, the oxidation of adsorbed  $\text{HCOOH}$  was performed in either  $\text{O}_2$  or  $\text{He}$ . Third, the UV irradiation was interrupted for various periods to allow O atoms to equilibrate between the lattice and the surface, assuming that surface O atoms were consumed by the reaction. In  $\text{He}$ , the  $\text{HCOOH}$  oxidation occurred to an extent that could not be due to traces – thoroughly measured – of  $\text{O}_2$  in the  $\text{He}$  utilized. Replenishment of surface O atoms by bulk O atoms took place in the dark and its rate was enhanced by heating as was expected. These observations indicated the participation of surface O atoms in the oxidation of  $\text{HCOOH}$ . However, calculation showed that only about 3.7% of surface O atoms of  $\text{TiO}_2$  Degussa P25 coated on Pyrex glass was incorporated in the products of  $\text{HCOOH}$  under the conditions used. Note, however, that  $\text{TiO}_2$  Degussa P25 is prepared in a flame reactor, so that surface irregularities are supposed to be much less numerous than in the case of  $\text{TiO}_2$  samples prepared at lower temperatures.

## 7. Do pollutants interfere for their removal at ppbv levels?

Most often, to test a  $\text{TiO}_2$  powder, a  $\text{TiO}_2$  – containing coating or a photocatalytic reactor only one pollutant is used at ppmv level.

As aforementioned, indoor air contains many pollutants at much lower concentrations, that is, in the ppbv range. Therefore, competition between pollutants must be investigated by use of a mixture of several pollutants from a variety of chemical families in the ppbv domain. To my knowledge, very few reports [21,90–92] fulfill these conditions, perhaps because of the analytical difficulties when extremely low concentrations are employed. In a thorough study [92], performed with 10 organic compounds at 5–45 ppbv, no significant difference in the removed fraction was observed whether each compound was used alone or in the presence of the other nine compounds. This observation means that the number of photocatalytically produced active species was sufficient to degrade all

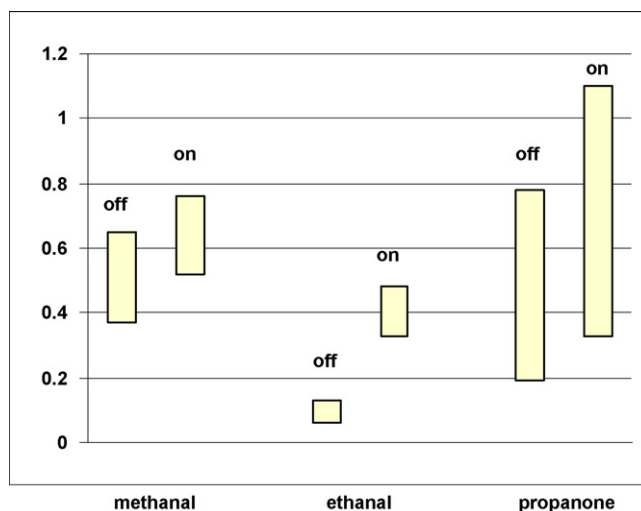


Fig. 2. Measured concentration ranges (in  $\mu\text{mol m}^{-3}$ ) for the  $\text{C}_1\text{--C}_3$  carbonyl pollutants indicated in an  $83\text{-m}^3$  non-airtight room when the purifier UV lamps were either off or on.

the compounds present in the mixture given the total concentration. The message is that, for indoor air, conditions can be found for the elimination of all pollutants and potentially their intermediate degradation products. By contrast, in the ppmv range, relevant to gaseous effluents but not to indoor air, the number of photocatalytically produced active species – which is determined *inter alia* by the irradiation characteristics, the type of  $\text{TiO}_2$ -containing coating, the amount of fully activated  $\text{TiO}_2$  – may be insufficient to efficiently remove several pollutants simultaneously or even one pollutant and its intermediate products of degradation, depending, of course, on the chemical reactivity and the contact time (e.g. [20,22,24,93,94]).

## 8. Potential danger linked to gas-phase carbonyl intermediate products

As any other advanced oxidation process, photocatalysis over  $\text{TiO}_2$  implies incorporation of O atoms and breaking of C–C bonds of organic pollutants. A reduced number of C atoms increases both the volatility and the mobility within the adsorbed water layers because of a size effect (see Section 2). On the other hand, intermediate products containing more O atoms than the initial molecules can be less volatile and have additional possibilities to create hydrogen bonds. From these opposite trends ensues a trade-off for each intermediate product determining whether it will be easily transferred to the gas phase because of a higher volatility and mobility or it will predominantly remain on the surface or within the adsorbed water layers.

Low-molar-mass carboxylic acids, which are near-end products of oxidation, are not easily released into the gas phase because of their high solubility (or even miscibility) in the adsorbed water layers. Consequently, they should not affect the indoor air quality in most cases. On the opposite, low-molar-mass carbonyl intermediate products can easily escape from the surface where they are formed. Accordingly, measurements of the concentrations in these compounds are required to determine the net effect of a photocatalytic air purifier regarding these hazardous compounds and hence whether this purifier is designed and used appropriately.

Fig. 2 shows results obtained in an ordinary room, that is, non-air tight, whose windows and doors were closed during the experiments [95]. The purpose was to compare the concentrations of formaldehyde, acetaldehyde and acetone when the purifier fan was always in operation to mix the air and the purifier UV lamps were

either off or on. The average (over 2-h periods) concentrations were measured several times with or without photocatalytic air treatment. Note that these carbonyl compounds were very likely not significantly photolyzed, since their absorption region was outside the 365-nm emission of the purifier UV lamps. For formaldehyde and acetone, the concentrations values with or without photocatalytic air treatment were found to overlap; nevertheless, the lowest concentration was found without air treatment and the highest was observed with air treatment (Fig. 2). Note that the wider range of acetone concentration compared with those of the other two carbonyls might have been due to the use of acetone as a common solvent in rooms in the same corridor as the test room. For acetaldehyde, the concentration domain of the treated air was even higher than that of non-treated air. In other words, for these three carbonyl compounds, the photocatalytic removal rate was on the average lower than the sum of the photocatalytic formation rate, the emission rate within the test room, and the rate of introduction into the test room from neighboring rooms and outdoors. However, the concentration domains with or without photocatalytic air treatment were relatively close (Fig. 2) contrary to fears of detractors of oxidation techniques for the treatment of indoor air.

In agreement with these results, formaldehyde and acetaldehyde, and in some cases acetone, formic and acetic acids, were found downstream when a photocatalytic prototype was fed with various realistic mixtures of common volatile organic compounds at ppbv concentrations and appropriate airflow rates [21,90–92].

The net effect of a photocatalytic air treatment upon the concentrations of low-molar-mass carbonyl compounds obviously depend on the room (air volume, air exchange, etc.) and on the purifier. This means that a given purifier must be employed only under conditions that ought to be indicated very precisely to the user. Progress in efficacy can be expected from the improvement of the UV lamps, the TiO<sub>2</sub>-coated materials and above all the design of the purifier in order to optimize both TiO<sub>2</sub> irradiation and TiO<sub>2</sub> exposure to air pollutants. Alternatively, the downstream use of a supplementary adsorbent or even a chemisorbent can be envisaged [92], but again it requires proper information of the client regarding the life-time of these additional devices.

## 9. Conclusions

Two essential data regarding indoor air seem to be generally not sufficiently taken into account when investigating, at the laboratory scale, the basic mechanisms and the possibilities of air purification/deodorization by TiO<sub>2</sub> photocatalysis. One datum is that the TiO<sub>2</sub> surface is covered by layers of water molecules because of air humidity. The second datum is that most air pollutants of interest with respect to purification and deodorization have concentrations comprised between fractions of ppbv to some tens of ppbv.

From these data, several conclusions can be drawn. It is suggested in this paper that the presence of well-organized layers of water adsorbed on TiO<sub>2</sub> has several effects. First, it hinders the approach of pollutants to the surface and hence dissociation of pollutants by mere adsorption is unlikely. Second, the formation reactions of radicals can be the same as those proposed for TiO<sub>2</sub> in liquid water; this means that •OH radicals can be formed by reaction of holes with H<sub>2</sub>O/OH<sup>−</sup> and surface O<sup>2−</sup>, and three-electron reduction of O<sub>2</sub> via the intermediate formation of H<sub>2</sub>O<sub>2</sub>. Third, a •OH radical formed on TiO<sub>2</sub> can easily replace a H<sub>2</sub>O molecule in the adsorbed layers and react there with the pollutants.

Although poorly reactive *per se*, O<sub>2</sub>•<sup>−</sup> can react with radical-cations formed by reaction of holes with certain pollutants. Formation of singlet molecular oxygen in TiO<sub>2</sub> photocatalysis remains debated in spite of recent more convincing studies. Various experiments have shown that labile surface O atoms can play a role in photocatalytic oxidations; however, this role seems minor.

On the other hand, the low concentrations of indoor air pollutants leads to the absence of significant competition between the removals of these pollutants under the conditions used in photocatalytic purifiers as it has been shown experimentally. However, despite these low concentrations, precaution is required concerning the use of these photocatalytic purifiers (as well as that of any purifier based on other oxidation methods), because the formation rate of intermediate products can be higher than their removal rate, which can result in an increase in their concentration even if it may remain relatively low. Therefore, measurements of the concentrations of low-molar-mass carbonyls under conditions as close as possible to the real use of purifiers are strongly recommended.

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